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Dielectric loss factor in electrically polarized polyvinylidene fluoride film electrets by TSDC

Devendra K Sahu[1]*, P K Khare[2] and R K Shrivastava[3]

[1]Department of Physics, Institute of Basic Science, Bundelkhand University, Jhansi-284 128, Uttar Pradesh, India

[2]Department of Postgraduate Studies & Research in Physics, Rani Durgavati University, Jabalpur-248 001, Madhya Pradesh, India

[3]Department of Physics, Bipin Bihari College, Jhansi-284 001, Uttar Pradesh, India

E-mail devendrasahu 2003@rediffmail.com

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Abstract Thermally stimulated discharge current (TSDC) in film of polyvinylidene fluoride(PVDF) was measured under various polarizing condition. The TSDC thermograms were recorded by reheating the samples at a rate of 3 °C/min. It was found that samples give rise to a peak around (100 ± 10°C). The peak position is not consistent with the polarization fields and temperatures. The activation energy associated with the peak is found to be ~0.62 eV. The dependence of TSD current and TSDC data on polarizing agents, i.e. field and temperature is explained on the basis of theoretical predictions. It can be considered that space charge polarization contributes significantly to the polarization of the polymer. The decrease in loss factor with increasing frequency can also be understood on the basis of space charge polarization. The dielectric loss factor has been evaluated and its variation with the angular frequency and forming polarization field (Ep) is reported.

Keywords : Thermally stimulated discharge current (TSDC), polyvinylidene fluorides, space charge polarization, dielectric loss factor

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1. Introduction

Thermally stimulated discharge currents (TSDC) technique is an effective tool in the measurement of dielectric properties of electret materials. The rapid growth of interest in recent years, in studying charge storage and transport phenomena in polymer electrets by means of techniques based on thermal stimulation, has been indicated by a number of publications [1-3]. Thermally stimulated discharge analysis of a polarized dielectric is commonly used to get an insight into its charging process, decay mechanism, thermal stability, activation energy and relaxation process. It also provides useful information about the molecular motion in dielectrics [2]. In this method, the specimen is polarized at high temperature by applying a dc field. The polarization frozen in by cooling the specimen with the dc field on TSDC, is observed by heating the thermoelectret [4,5] at a linear rate under short circuit conditions. The technique has shown that the total charge stored in a polymer electret and different mechanisms that contribute to the storage of charge, are very sensitive to the structure of electret forming material itself, because of the presence of different groups in main molecular chain [6]. Polyvinylidene fluoride (PVDF) is capable of storing a substantial amount of electrical polarization when subjected to a temperature field treatment. The PVDF films find extensive use in pyroelectric and piezoelectric devices. Knowledge of the dielectric loss behaviour is important because of the possible technical application of polymers for insulation, isolation and passivation in microelectronics. Dielectric relaxations of PVDF have been investigated by several researchers and summarized by Lovinger [7].

For dipolar relaxations, the maximum dielectric loss occurs at the resonant frequency, which is inversely proportional to the relaxations time (τ) of the dipoles at the temperature of measurement (T) and τ is given by

$$\tau = \tau_0 \exp(E_a/kT), \quad (1)$$

where τ_0 is the pre-exponential constant, E_a the activation energy and k is Boltzmanns constant.

* Corresponding Author

From eq (1) we have

$$\ln \tau = \ln \tau_0 + E_a/kT \tag{2}$$

which ultimately yields [8]

$$\ln \tau = \ln \int_{t'=t(T)} i(t')dt' - \ln i(T), \tag{3}$$

where $i(t')$ is current at a time t' and corresponding temperature is T. From eq (2), a plot of ln τ *versus* $1/T$ gives a straight line; the slope and intercept of this line serve to determine the value of E_a and τ_0. The integration part of eq. (3) can be estimated graphically with fairly good accuracy, from the TSDC curve. Once τ_0 and E_a are known, τ at any other temperature can be calculated by using eq. (1).

The area under the TSDC curve gives the charge $Q(T_p, E_p)$ stored in a dielectric after polarization. It can be expressed in terms of steady state dielectric constant (ε_s) and high frequency dielectric constant (ε_∞) of the material [6-8]

$$Q(T_p, E_p) = (\varepsilon_s - \varepsilon_\infty) C_0 E_{eq}, \tag{4}$$

where C_0 is the air capacitance of the sample assembly and E_{eq} is the equivalent electric field which will give the same charge Q (T_p, E_p). The Debye equation for dielectric loss given by

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{(1+\omega^2\tau^2)} \tag{5}$$

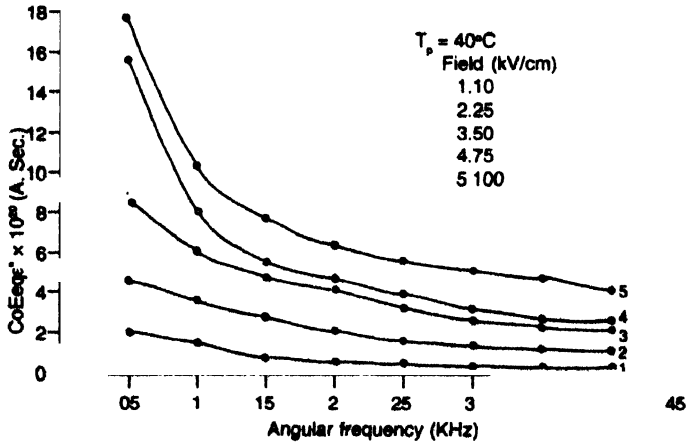

Figure 1. Variation of dielectric loss factor $C_0E_{eq}\ \varepsilon''$ with angular frequency for samples prepared at different E_p and constant Tp = 40°C.

can now be rewritten as

$$C_0 E_{eq}\varepsilon'' = \frac{Q(Tp, Ep)\,\omega\tau(Tp)}{1+\omega^2\tau^2(Tp)} \tag{6}$$

Using the value of Q and $\tau(T_p)$ obtained from the TSDC curve, the factor $C_0\ E_{eq}\varepsilon''$, which is proportional to the dielectric loss ε'', can be evaluated and represented as a function of ω (Figures 1, 2).

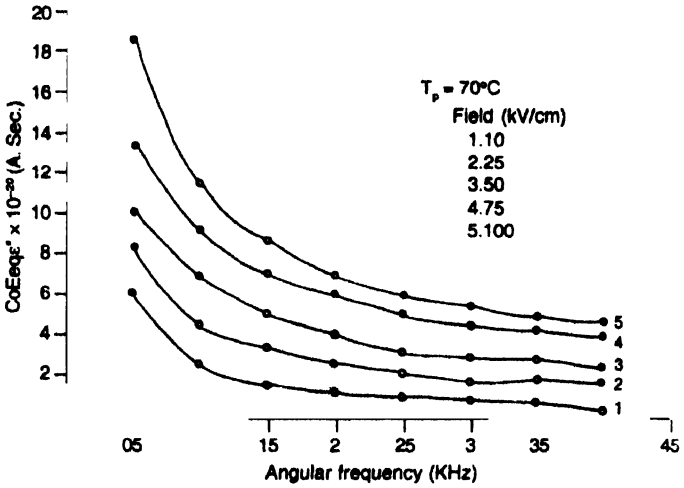

Figure 2. Variation of dielectric loss factor $C_0E_{eq}\varepsilon''$ with angular frequency for samples prepared at different E_p and constant Tp = 70 °C

2. Experimental details

Commercial polyvinylidene fluoride (PVDF) used in the present investigation has been procured from Glaxo Laboratory, Mumbai. Chemically pure PVDF were weighed, then dissolved in dimethyl formaldehyde in 30% solution. This solution was stirred at 40 °C in a magnetic stirrer for a minimum four hours. Thereafter, the homogeneous solution thus obtained was poured over the glass plate, heated in the mercury pools kept inside the oven. Great care was taken to avoid air bubbles during the setting of polymer solution over the plates. The solvent was made to evaporate for a minimum of 12 hrs. The glass plates were taken out carefully. Film was detached from the glass plate using a sharp edge knife or blade. The film was preserved between paper leaves so that it is not damaged. The film so formed was then outgassed in air at 50°C for 24h, followed by room temperature outgassing at 10^{-4} torr for a further period of 24h.It was then gently lifted off from the glass plate. Both surface of the samples were then vacuum aluminized over a central circular area of 4.0 cm^2. The sample were polarized for 90 min with polarizing field and then were cooled, under the application of field, to the appropriate temperature. Afterwards, the field was switched off and the sample was short-circuited for an arbitrary time of 10 min, so as to remove the frictional and stray charges present. Thereafter, the sample was heated at a uniform rate of 3 °C/min from room temperature to about170°C and the current was recorded by a 600C Keithley electrometer which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise. The field was applied from a high voltage unit EC4800D.The temperature of the sample was recorded with a pre-calibrated thermocouple attached in close neighborhood of the sample. The thickness of the sample was of the order of 20μm, which was estimated by measuring the capacitance of the

fabricated sandwiches. The depolarization kinetic data, *i.e.* activation energy, charge released and relaxation time for the observed peaks have been calculated using initial rise method [9,10] (Tables 1a, 1b).

Table (1a). Values of Im, Q, Ea, τ_0 and $\tau(Tp)$ calculated by Bucci plot method (Tp = 40°C)

Ep (kV/cm)	Q (coul.)	Im(Amp.)	Ea (eV)	τ_0 (sec)	τ (sec)
10	3.2×10^{-7}	2.0×10^{-10}	0.612	6.76×10^{5}	4.06×10^{12}
25	4.0×10^{-7}	2.6×10^{-10}	0.623	4.78×10^{6}	4.63×10^{11}
50	8.0×10^{-7}	3.6×10^{-10}	0.621	7.85×10^{7}	7.61×10^{12}
75	9.0×10^{-7}	5.0×10^{-10}	0.622	8.24×10^{6}	2.22×10^{12}
100	9.8×10^{-7}	6.6×10^{-10}	0.623	9.55×10^{8}	9.01×10^{12}

Table (1b). Values of Im, Q, Ea, τ_0 and $\tau(Tp)$ calculated by Bucci plot method (Tp=70°C)

Ep (kV/cm)	Q (coul.)	Im(Amp.)	Ea (eV)	τ_0 (sec)	τ (sec)
10	3.0×10^{-8}	6.0×10^{-10}	0.584	5.78×10^{6}	2.07×10^{15}
25	3.8×10^{-8}	8.0×10^{-10}	0.597	4.47×10^{7}	6.06×10^{16}
50	5.6×10^{-7}	1.2×10^{-9}	0.618	9.32×10^{8}	2.38×10^{16}
75	6.8×10^{-7}	2.0×10^{-9}	0.627	2.46×10^{7}	1.00×10^{17}
100	8.0×10^{-8}	2.6×10^{-10}	0.629	3.57×10^{7}	7.21×10^{16}

3. Results and discussion

The thermally stimulated depolarization current (TSDC) characteristics of polyvinyledene fluoride (PVDF) sample polarized at polarizing temperatures 40 and 70 °C with 10,25,50,75 and 100 kV/cm polarizing fields. A broad peak is observed around 100 ± 10 °C in all cases. The magnitude of peak current increases with increase in polarizing fields and temperatures (Figures 3, 4). However, shifting of peak position with polarizing fields was not consistent.

Polyvinylidene fluoride (PVDF) is of fundamental interest for its different crystalline phases and phase transitions. PVDF can exist in five distinct crystalline structures depending on the formation conditions of the polymer. Four of these phases designated as α, β, γ and δ respectively by form I, II, III and IV are stable at room temperature, a fifth form ε could exist just below the melting point [11]. The α - phase of PVDF crystallizes from the melt [12]. The β-phase is normally obtained by mechanical deformation of α-form [13, 14]. Growth from solutions such as dimethyl sulfoxide or dimethyl acetamide usually leads to ν form [15]. PVDF is inherently polar. The hydrogen atoms are positively charged and the fluorine atoms negatively charged with respect to the carbon atom in the polymer. The net moment of a group of molecule in a liquid region of PVDF will be zero in the absence of an applied field because of random orientation of individual dipoles. PVDF has attracted considerable attention due to unique electoactive properties included by high field exposure.

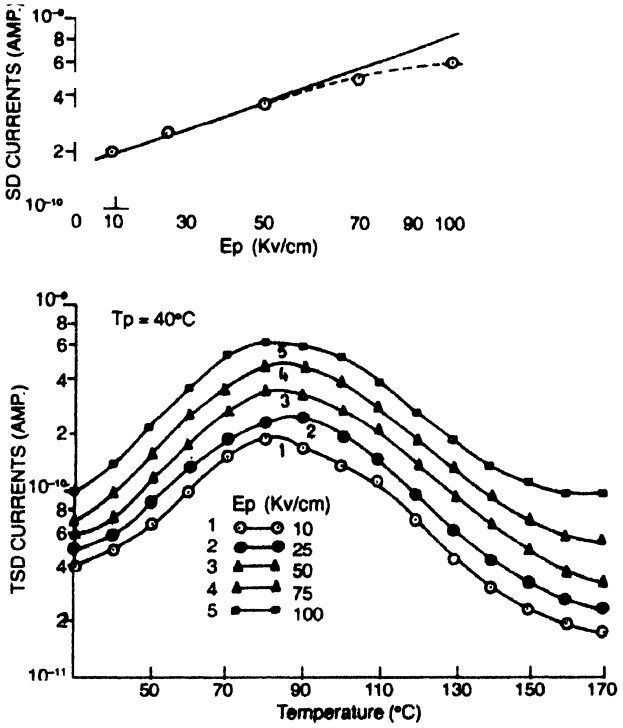

Figure 3. Thermally stimulated depolarization current thermogram for polyvinyledene fluoride at constant polarizing temperature (Tp = 40°C) with various polarization fields at heating rate 3 °C/min.

The electrification of the polymers takes place due to one or more of the following mechanisms operating simultaneously when it is subjected to dynamical, mechanical or thermal treatment with or without the static electric fields :

(i) space charge injected into the dielectric by surface breakdown between the dielectric and the electrode,

(ii) space charge injected from the electrodes,

(iii) space charge caused by migration of charge carriers over macroscopic distances,

(iv) electronic or ionic dipole caused by migration of charges over microscopic distances, and

(v) orientation and permanent dipoles.

When an electret is heated to obtain the TSD current, the peak which generally appears near T_g is either due to randomization of the oriented dipoles or due to release of charge carriers from traps. Generally, polymers contain a small number of free charge carriers, *i.e.*, ions, electrons or both [16]. During electret formation, the carriers move comparatively free in the

direction of the applied field over microscopic distance before they fall into deep traps from which they can be released only on receiving sufficient energy. In the present investigation, TSDC thermograms exhibit a broad peak. This peak gets centered

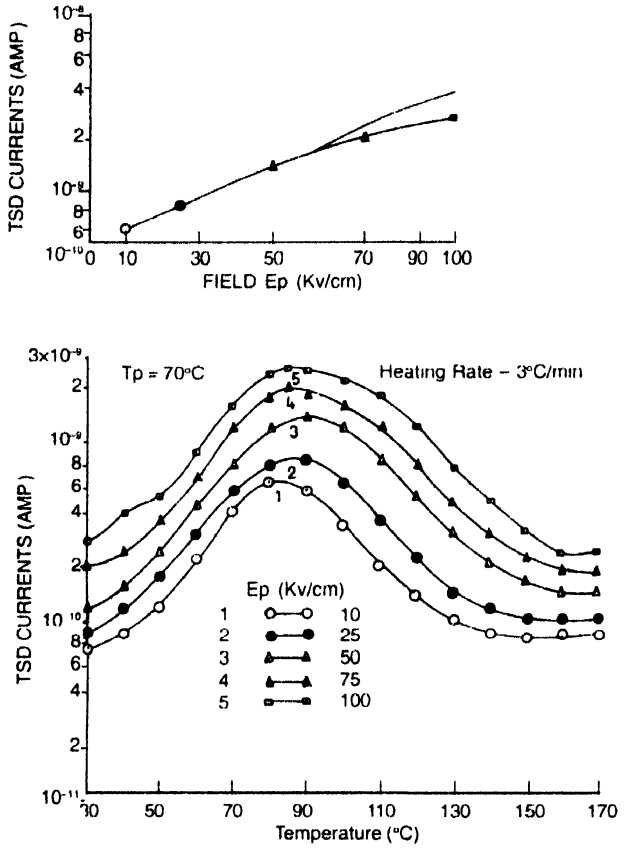

Figure 4. Thermally stimulated depolarization current thermogram for polyvinyledene fluoride at constant polarizing temperature (Tp=70°C) with various polarization fields at heating rate 3 °C/min.

around 100 ± 10 °C. Broad peaks represent presence of multiplicity of relaxation mechanism. The multiplicity of relaxation in PVDF may be because of presence of trapping levels of different depths. Two peaks were reported for PVDF [17]. The first peak reported at 30 °C (related to the charging temperature) and at 52°C due to release of charges trapped at crystalline / amorphous boundaries. The appearance of peak in the high temperature region, imply that the injection of ions may be significant in this polymer .It is also possible that PVDF contains a high number of impurity molecules prior to field treatment and these molecules are dissociated into various ionic species by combination of the high internal and external fields. The charge trapping in a polymer takes place at the molecular main chain, the side chain and at the interface of crystalline and amorphous regions of the polymer [18-20]. The high field applied during electret formation, may also produce some additional trapping sites. Since PVDF is a semicrystalline polymer, the charge storage and transport in it, is expected to be dominated by various localized levels in the amorphous regions and also at the crystalline amorphous boundaries. Further, since it is a polar polymer, the probability of the presence of intrinsic charge carriers in it, is also sufficiently high, particularly at high temperatures. Incidentally, in heterogeneous hetero electrets of PVDF, these charges will mainly pile up at the phase boundaries. They are supplied there by unequal ohmic conduction currents, within the two phases (Maxwell-Wagner charging). These carriers are also likely to be trapped in different trapping sites leading to space charge effects which fundamentally influence all the charging and transport processes. Their high concentration often enables them to contribute discernly to the short-circuit thermally stimulated discharge currents.

The charge released during TSDC has been calculated by extrapolating the curves to temperature axis and its values are shown in Tables (1a, 1b). The dielectric loss factor has been calculated using eq. (6) by substituting different values of ω

The variation of dielectric loss with angular frequency is shown in Figures (1, 2). At lower frequency, there is considerable increase in the loss factor with electric field With no external field and in thermal equilibrium conditions, detailed balancing ensures that the energy loss is incurred every time The dipole relaxes into a new position, it is fedback into the system by thermal phonons to provide the extra energy for the corresponding upward excitation. Therefore, there is no net loss or gain of energy in the system. The application of an external electric field changes the energy balance favouring transitions in one direction and opposing those in the other This results in a net charge in polarization. Polarization in polar dielectrics occurs mainly by orientation of dipolar species. As the frequency of ac field is increased, the dipoles find themselves unable to keep pace with the fast changing field. As a result, the value of losses drops.

The variation in loss values suggests the net effect of some internal field within the polymer alongwith the external ac field The increase in losses at low frequency could be associated with the polarization of the trapped charge carriers. With the increase in frequency, polarization decreases and becomes vanishingly small at high frequencies. The decrease in losses with frequency also seems to show the decrease in the number of charges and delay in settling of dipoles due to availability of very short time in one half cycle of alternating voltage. The general expression for dielectric loss is given by the equation

$$\tan\delta = \frac{\omega^2\tau^2(Gin+S)+Gin}{\omega\left\{S\tau+Cg\left(\omega^2\tau^2+1\right)\right\}}, \qquad (7)$$

where Gin is the conductance for the residual current. From eq (7)

$$\lim_{\omega\to 0}\tan\delta = \infty,$$

$$\lim_{\omega\to 0}\tan\delta = 0.$$

Differentiating eq. (7) with respect to ω and then equating the derivative to zero, it is possible to obtain the value of ω of the frequency corresponding to maximum loss. The increase in losses at low frequency may be ascribed to interfacial polarization involving ionic movement. With the increase in frequency, interfacial polarization decreases and becomes vanishingly small at high frequencies. Polyvinylidene fluoride is a polar polymer. The decrease in loss values with increase in frequency verifies the fact that for polar polymers, the initial loss value is high.

The decrease in loss values with increasing frequency can also be understood on the basis of space charge polarization. Space charges arise due to inhomogeneity in the electrical properties of a dielectric. In the presence of field, the charges (electrons or ions) may tend to pile up at the crystalline-amorphous boundaries. At lower frequencies, it is possible for the space charge formation to be in phase with the variation of the ac field. This however, is not possible at higher frequencies. Hence, the space charge is noticeable at lower frequencies resulting in a high initial value of losses as observed in the present investigation.

4. Conclusion

The analysis of various results indicates that the phenomena responsible in the present case, are due to simultaneous dipolar reorientation by the molecular motions associated with the side chains and space charge effects resulting from trapping of injected charge carriers in energetically distributed traps. The space charge mechanism appears to be the controlling mechanism.

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